Oil-Absorbing Polymers

H. E. Marsh, Jr.

Propulsion Division

A new research program has been started to develop technology needed to make practical use of a well-known characteristic of elastomeric cross-linked polymers. Such polymers, of which class modern solid-propellant binders are members, absorb large amounts of compatible solvents, and yet remain solid. Two goals are being considered in this program. One goal is a material that can be used as a dietary additive which will selectively absorb fats and oils in the digestive tract and hold them until elimination, thus preventing their assimilation. The other goal is a material that can be used in oil-slick mop-up operations. This article presents the interim results on the formulation and testing of three polymer types. Performances amounting to oleic acid absorption of up to 20 times the dry polymer weight have been measured. Higher values are expected. Both mineral oil and a cooking oil are also absorbed, but to a smaller extent.

Introduction

The chief distinguishing structural feature of the class of polymers known as thermosetting is that the component polymeric molecules are tied together in a three-dimensional network. The average length of polymer chain between cross-linking (interconnecting) sites, together with the flexibility/stiffness character of the chain material, determines the mechanical properties of the polymer. Regardless of chain flexibility, highly cross-linked polymers are rigid. On the other hand, polymers with long chains between cross-links are rubbery, providing those chains are flexible. Another characteristic of the latter type of polymer that has been known and studied for a long time is its ability to absorb extremely large quantities of compatible solvent and yet remain solid.

A new research program has been undertaken to take practical advantage of the high absorption capacity of suitably prepared network polymers. Two goals are being considered. One goal is the development of polymers with a high affinity for the fats and oils common in foods that, being otherwise harmless, could be used as a dietary additive for the control of fat assimilation. Being inert, the polymer would pass through

the digestive tract absorbing and retaining fats and oils, including cholesterol, for elimination. The other goal is the development of similar materials that will be useful in oil-slick mop-up procedures.

Approach

The technology adopted to make high capacity absorbing cross-linked polymers is based on knowledge gained in work with solid-propellant binders (References 1 and 2). The aim is to make polymers that are cross-linked, so that they will remain solid even though swelled by large quantities of absorbed oil, but at the same time provide an average chain length between the cross-link sites as large as possible to obtain maximum capacity.

Preparation

There are two steps in the process: synthesis and extraction. The synthesis step consists of mixing together appropriate quantities of several polyfunctional ingredients, along with a polymerization catalyst, and causing them to polymerize by means of heat. Network polymer theory is used to calculate the ratios of ingredients that should yield polymers with the desired characteristics. The ideal composition is near the incipient gelation boundary (Reference 1). However, in practice, this calculation serves only as a starting point for an empirical search. The necessity for empirical experimentation is caused by the fact that polymer formulations with the best absorption capacities are so lightly cross-linked that they are almost liquids instead of solids. Factors not accounted for in the theoretical calculation, such as incomplete reaction, non-ideal functionality distribution of the components, and side reactions, all interact with the sensitivity of such formulations to cause an unpredictable shift of the real solid/liquid boundary from the theoretical one. Thus, in the empirical search for a good formulation, a series of samples are made at the same time with composition ratios varying over a range estimated to bound the problem. A satisfactory series will yield some liquid and some gelled polymers. Often, one or more additional sets must be run, either to find the correct range or to refine the desired point.

Gross distinction between liquid samples and solid ones is made by visual observation of the flow properties of the polymer. However, some samples that appear to be solid turn out later to be only high molecular-weight liquids. This is evidenced by total extraction in the next process step.

Another characteristic of the desired lightly cross-linked polymer (in practice, but not necessarily in theory) is that it consists of two separatable fractions. The desired fraction is the lightly cross-linked gel, or solid. In homogeneous solution with the gel is the sol, or liquid fraction.

The latter is a polymerized material that did not reach the size and complexity necessary for it to become part of the gel. Repetitive solvent extraction of a fresh polymer removes the sol fraction, leaving a residue of "dry" gel. Soxhlet extraction is used in the present work to carry out this operation automatically.

Screening and Evaluation

The criterion for a good polymer is its capacity to absorb a large amount of oil (of a type critical to the objectives of the program). Although the main stress in the program is in the absorption of biologically important oils and fats, a laboratory grade of mineral oil is used as one of the test materials, as a model for the oil-slick problem. In private communication, Dr. David Blankenhorn of the USC School of Medicine recommended the following compounds for testing the feasibility of the fat assimilation control concept:

(1) *Carboxylic acids:* palmitic acid, oleic acid, myristic acid, butyric acid, and a C-22 acid.

(2) *Alcohols:* cholesterol.

(3) *Esters:* triglycerides of palmitic and oleic acids, and the palmitate of cholesterol.

Since it would be very inefficient and expensive to test each new polymer with all of these materials, the oleic acid was the only one selected for the screening tests because it is the least expensive and is a liquid at room temperature. The other compounds will be used in the evaluation of polymers selected in the screening tests.

Because of experimental difficulties, the accuracy of the measurement of the absorption capacity is limited. The current procedure starts with the immersion of a weighed quantity of polymer in a volume of the test liquid. It is examined daily, and when the polymer appears to have stopped swelling, it is removed and drained (most of the surface liquid is removed by blotting with tissue). The last operation is where the uncertainty lies, because of the lack of uniformity of surface configuration from sample to sample, and also because the structural weakness of some swollen gel samples gives difficulty in carrying out the operation. Lack of accuracy in these measurements is not critical in the screening tests, however. As will appear in the results below, the differences in capacity are large in comparison to such errors in measurement.

Polymer Types Investigated

For all of the past work, and for as long as it continues to be practical, the urethane reaction is the adopted means of curing. Since this is the chief cure system used in the fabrication of JPL propellants, a wide variety of potentially useful materials are readily available.

An anticipated major factor in the absorption capacity of network polymers is the chemical nature of the chain-forming ingredient. In advance of experimentation, hydrocarbon chains were expected to have a greater affinity for the oils in question because of the long-chain hydrocarbon characteristic common to them. Several hydrocarbon prepolymers are being tested: some unsaturated (polybutadiene), and some saturated (similar to ethylene–propylene copolymers). A common polyether (polypropylene oxide) is also being tested, primarily because it is not hydrocarbon. Polyesters are under consideration; however, their stability in the digestive system may be in question.

Interim Results

Formulation Studies/Screening Tests

Three polymer systems have been investigated: unsaturated hydrocarbon, mixed saturated/unsaturated hydrocarbon, and polyether. Reasonably good absorption of oleic acid has been obtained with each system. The highest absorption capacities measured so far for the above three systems were, respectively, 1390, 1210, and 2050% oleic acid absorbed, based on the dry weight of the polymer.

In many cases, the formulation series sets did not correlate closely with theory. This was expected because no effort was made to control reaction conditions carefully for this purpose. The desired practical results were achieved, however. An example of a formulation series in search of a good absorber is given in Table 1. This set of samples was a series of unsaturated hydrocarbon formulations in which all factors except the hydroxyl-to-isocyanate ratio R were held constant. According to theory, the gel point R for this set should be 1.25. Two samples were unable to produce a gel because R was too high. The variation in sol/gel ratio and absorption capacity of the two solid products are in the expected directions. If this particular system were to be selected for further work, another series would be run in which a number of R values between 1.32 and 1.52 would be tried. A formulation having maximum absorption capacity should be found in that range.

Table 1. Effect of formulation parameters on absorption capacity

Sample number	Hydroxyl-to-isocyanate ratio	Product	Sol/gel ratio	Oleic acid absorbed, %
101	1.16	Solid	0.35	830
102	1.32	Solid	0.69	1380
103	1.52	Liquid	—	—
104	1.79	Liquid	—	—

Testing Oils and Solvent Polymerization

In most of the past work, only oleic acid was used in absorption screening tests. To broaden the screening tests, it was decided to try, as an inexpensive model for the ester-type oils, a commercial cooking oil. Cooking oils are refined natural mixtures of triglycerides from vegetable sources. Wesson oil was chosen. It was also decided to include mineral oil as a model for strictly hydrocarbon materials. It is important to mention in this regard that mineral oil was used in the first exploratory tests. An absorption capacity of over 800% was attained then, using an unsaturated hydrocarbon polymer.

First tests with the Wesson and mineral oils were made with polyether polymers. The results indicated that the polymers' capacities for these two oils were between about one-fiftieth and one-fifteenth of their previously measured capacities of oleic acid. These results are preliminary; however, if they are representative, they show that the unreacted carboxyl on the oleic acid molecule contributes largely to its solubility in polyether polymers.

The test was repeated with two unsaturated hydrocarbon polymer samples that had been in storage for many weeks. Theoretically, these oils and hydrocarbon polymer should be compatible. The results were about the same as with the polyether polymers; however, the capacity was much lower than the 800% found previously with a hydrocarbon polymer.

Two possible explanations are proposed for this undesirable result. The first is that the unsaturated hydrocarbon polymers stored for some time in air may have undergone oxidative cross-linking, similar to the process which hardens paints and varnishes.

The second explanation is that the recently tested polymers were made in bulk, whereas the earlier, more successful polymer had been made in 50% xylene. Network polymers made in solution would be more extended (would have fewer chain entanglements) and as a result might be more extensible even after drying. Two fresh sets of hydrocarbon polymers were made in solution; one polymer was unsaturated and the other was mixed saturated/unsaturated. Absorption tests have not run their full time yet, but absorption capacity for mineral oil has improved by a factor of about 2½, and even higher for Wesson oil.

Polymer Reinforcement

The mechanical weakness of some swollen gels has caused difficulty in handling during testing. Mainly for the purpose of expediting screening tests, the formation of polymers on reinforcing substrates was investigated. A secondary aim was to demonstrate that greater strength

could be provided, when needed in application. A good substrate must reinforce the polymer during absorption without restricting the absorption capacity appreciably.

The substrate materials tried were cotton fibers, pulled from cosmetic cotton batting, nylon tow, and fine-mesh nylon screen. The very high surface area of these materials proved troublesome in two respects. Formulations with as high as 3 to 5% of loose fibers appeared to be too highly loaded for useful processing. Interference with curing, probably caused by undesirable chemical activity at the surface, was also encountered. Substrate loadings in the range of 0.5% were found to be more suitable with respect to both problems.

Substrate testing is not completed. However, for testing purposes, the nylon screen with a thin film of polymer appears to be a practical arrangement. One such sample exhibited an absorption capacity of 1460%. To curtail the impairment of curing, it is planned to pretreat the screen with tolylene diisocyanate, the curing agent.

Time-Consuming Operations

Another factor, besides the lack of reproducibility in removal of surface oil in absorption tests, which has contributed to uncertainty in the data, is the length of time required for complete absorption. Although the required time has not been determined, it appears to be of the order of two weeks. The extraction operation also is slow; it takes five days.

Recent tests have shown that moderate temperature elevation increases the rate of absorption considerably. Heretofore, testing has been done at room temperature, which has been ranging from 17°C (62°F)[1] to 24°C (75°F). A study is currently being carried out at two temperatures: 38°C (100°F) and 49°C (120°F). Preliminary data indicate that absorption values obtained previously in one to two weeks at room temperature were achieved in two days at 49°C (120°F).

The preparation of thin polymer samples on nylon screen substrates is expected to increase the rates of both extraction and absorption because the reduction in, and better control of, diffusion distance.

The elevation of temperature will also be investigated in the extraction operation. This will be accomplished by the substitution of the higher boiling solvent xylene for benzene.

[1]Where applicable, the International System of Units is stated first, followed by the customary units in parentheses. In each case, the value in parentheses represents the measured unit.

Questions of Polymer Stability

Occasionally, samples which have undergone extraction, yielding a solid product, seemed to have disappeared in the absorption test. This should not occur because a solid residue from extraction is positive evidence of a cross-linked polymer. The most likely explanation is a chemical displacement of previously reacted hydroxyl in the polymer by the carboxyl group on the oleic acid. Such a reaction would simultaneously result in the introduction of an extra monofunctional component and a shift in the stoichiometric ratio, both of which would reduce the extent of cross-linking.

An experiment was started to investigate the possibility of polymer size degradation by reaction of oleic acid into the polymer. The experiment was based on the often used principle of determining the molecular weight (or size) of dissolved polymers by viscosity measurement. One of the previously made polymer samples that had remained a liquid after cure was dissolved in a plasticizer, and oleic acid was added so that the final solution had 21% polymer and 12.5% oleic acid. The solution was stored at room temperature, and the viscosity was measured once or twice a week, along with the temperature, in order to normalize viscosity and eliminate temperature as a parameter. After a period of a month, no change in the viscosity of the solution was detected. If a significant amount of the suspected reaction had occurred, the viscosity of the solution would have dropped because of the resulting decrease in molecular weight.

As far as this experiment has gone, there is no evidence that oleic acid degrades the polymer. The question of disappearing gels is still open. However, there is an indication that one factor in the intended environment will not cause degradation of urethane-cured polymers.

Conclusions

Preliminary results indicate that:

(1) All three polymer types tested (unsaturated hydrocarbon, mixed saturated/unsaturated hydrocarbon, and polyether) have good absorption capacity for oleic acid. The highest capacities measured range from 12 to 20 times the dry weight of the absorbing polymer. None of these polymers have been optimized.

(2) The absorption capacities for both mineral oil and Wesson oil by these polymers appear to be considerably less than for oleic acid.

(3) Solution polymerization produces polymers that either have higher capacities or more rapid absorption rates than bulk polymerization does.

(4) Carboxylic acids, as represented by oleic acid, do not appear to degrade the urethane-cured polymers investigated.

Future Work

Future and continuing tasks in this program are listed as follows:

(1) Formulating and processing studies of the three polymer types will be continued to produce optimum products. Technical improvements, including substrate reinforcement and solvent polymerization, will be used. Reproducibility of preferred formulations will be investigated.

(2) The absorption capacities of the selected formulations of each polymer type for oleic acid, Wesson oil, and mineral oil will be measured.

(3) Absorption of the other selected biologically important fats and oils will be studied.

(4) The general technology of producing oil-absorbing polymers will be investigated. Modifications of the types of polymers under study, as well as new types, will be tried.

(5) In consultation with medical experts, plans for future investigation will be made. Subjects to be studied must include the measurement of the stability of high absorbing polymers in simulated environments, whether or not toxic effects can be discovered, and the efficiency of absorption in the simulated environment.

References

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